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Abstract

For many years, the accumulation of material deposits on the surface of the die, commonly referred to as *die build-up*, has been a major obstacle for efficient processing of polyolefins. Indeed, extrusion lines ultimately have to be shut down as a thermally-degraded waxy deposit starts to affect the extrudate quality. In order to gain systematic insights into this multidisciplinary problem, *a new technique* has been developed. It confirmed that die build-up *is related to die-swell*, which provides a medium for transporting pigments, degraded polyolefin, and other materials towards the die surface. Several solutions will be proposed based on the use of fluoropolymer-based processing additives (commonly referred to as PPA) and/or the use of LLDPE's produced with Exxpol® technology. This work is the result of *a fruitful cooperation between Dyneon N.V. and Exxon Chemical.*

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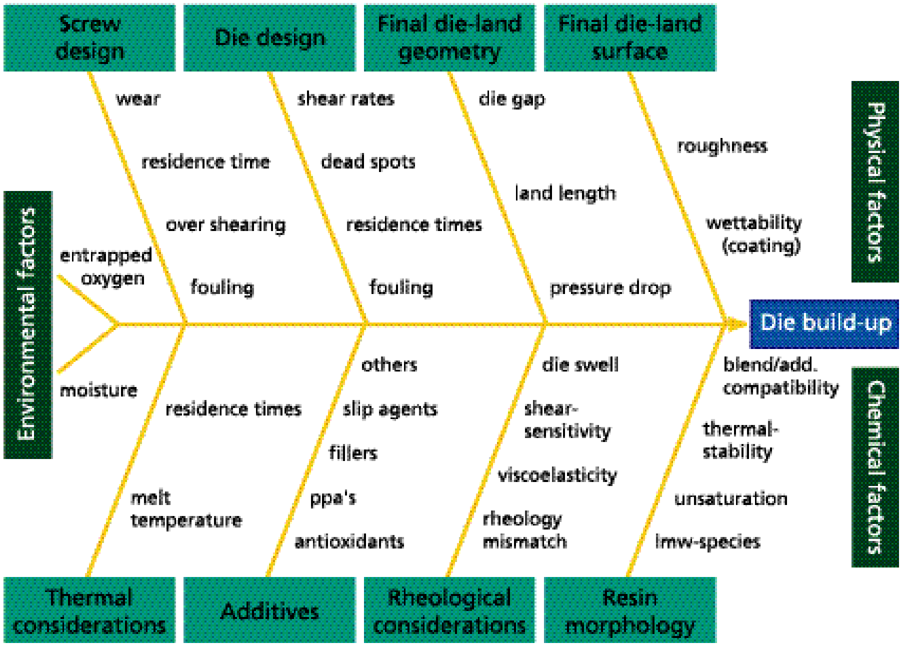
1. Introduction

Die Build-Up (DBU) is the progressive deposition of components of the extrudate exiting a die during extrusion operations. It occurs with many polymers, on virtually all converting techniques such as blown film extrusion, coating, pipe and profile extrusion. Excess DBU will be brought in contact with the external die surface, adhere to it, slowly accumulate around the die exit where thermal oxidation takes place. After a while, a portion of the DBU attaches itself to the extrudate, breaks off, is carried downstream on the product, and the phenomenon starts over again. DBU gives rise to surface irregularities affecting aesthetic, optical and mechanical properties of the extrudates. These effects worsen with time to the extent that extrusion has to be stopped for die cleaning, at the expense of production cost-efficiency.

Although it is a significant problem, very little is known in the literature and in the industry practice about the fundamental mechanism of die build-up. While there is a general consensus on the definition of DBU, there are still many attempts to develop a theory capable to predict accurately and reliably when and how much DBU will occur [1-7]. Film producers, resin suppliers, and machine manufacturers have their own theories based on limited observations. A recent paper by Gander and Giacomin [3] gave a comprehensive review on the subject.

DBU is undoubtedly a multidisciplinary problem, best illustrated in an Ishikawa-type diagram shown in Figure 1.

Figure 1
Die build-up is a multidisciplinary problem



It illustrates the three basic factors that influence DBU : (1) chemical factors related to resin composition, (2) physical factors related to the processing equipment, and (3) inherent environmental factors like oxygen or moisture. Many parameters in this diagram are interrelated, with possible synergistic or antagonistic effects. Therefore, apparently contradictory conclusions are sometimes reported (thermal stability issues suggest that higher temperatures lead to faster DBU, but the problem is often worse for blown film than for cast despite the higher extrusion temperatures in cast. Adding metal stearates has both positive and negative reported effects, etc.). In fact, DBU has been tackled by different people with different interests and concerns. This explains the lack of a universal solution and the use of a trial and error approach for practical, immediate problem solving. Out of these observations, two directions can be delineated.

1.1 Composition analysis

Composition analysis demonstrated that DBU consists of organic and inorganic low-molecular weight materials that had migrated to the die surface.

These species are incompatible with the polymer, and encompass :

- low molecular weight waxy materials present in the initial resin or resulting from thermal degradation in the extruder. This highlights the need for
    - good control of the extrusion process (residence times, shear rates, etc.), and
    - a proper stabilization package.

- organic or inorganic additives. The latter can also trigger degradation reactions.

Differences in surface energy will be the driving force for this migration, and die-wall nature and cleanliness will therefore also play a role. Reduction in adhesion at the metal - polymer interface might decrease the production rate of DBU.

1.2 This migration is influenced by die-swell

A material that swells a lot will have a greater propensity to accumulate at the die exit and drag already accumulated material onto the moving web. High die-swell generally results from more intense processing conditions, enhancing therefore flow-induced migration of waxy components at the die wall. ***In this respect, die swell might be a major vehicle for DBU, even if it is not the root cause of the phenomenon.***

As a matter of fact, all die geometry changes resulting in die-swell reduction (increasing die land length, increasing die gap, flaring the die exit, etc.) are already patented methods for DBU reduction. Not all these parameters can be manipulated to the same degree. Die opening for example is fixed by the dimensional requirements of the extrudate and the polymer type (small die gap to extrude LDPE, larger for LLDPE).

However, the magnitude of die-swell can also be controlled by a proper viscosity/elasticity balance of the polymer melt. This suggests that molecular structure (molecular weight distribution, presence/absence of long-chain branches) can also be tailored in order to reduce DBU, which is of course much more pertinent from the point of view of a polymer producer. In addition, the use of fluoropolymer-based processing additives is also expected to result in a lower die-swell and a reduced surface energy of the metal surface for a given polymer under certain process conditions. It is our intention to develop both aspects in this paper.

2. Newly developed test methods

2.1 Tracking DBU formation

Exxon Chemical has developed a test method in order to quantify and accelerate DBU on a down-sized extruder, still representative of processing conditions encountered in real life production. The method had to pass two critical success factors:

- product differentiation had to be demonstrated within an acceptable time (2 hours)
- shear history and temperature profile had to be realistic as compared to actual production conditions.

The method consists in using an image analysis technique to monitor the surface of a flat die during the extrusion process. Such a device enables an easy visual observation of the die lips, and the die deposit is less easily taken away by the continuous polymeric flow than with other die geometries. A flat die can be opened for cleaning and studying the surface after testing. Processing conditions, such as shear stresses, output and melt temperature have been optimized in order to achieve highest die-swell and hence accelerate DBU. Between each test, a thorough cleaning protocol was followed. A video recorder follows the accumulation of DBU at the die lip. Images were processed using GlobalLabImage® software, providing as test outputs the rate at which accumulation occurs and an assessment of the deposit in function of extrusion time. This test method is especially suitable to investigate pigmented polymers. Figure 2a. describes the settings used during our tests. Figure 2b. illustrates how die build-up accumulates.

Figure 2a
Die build-up

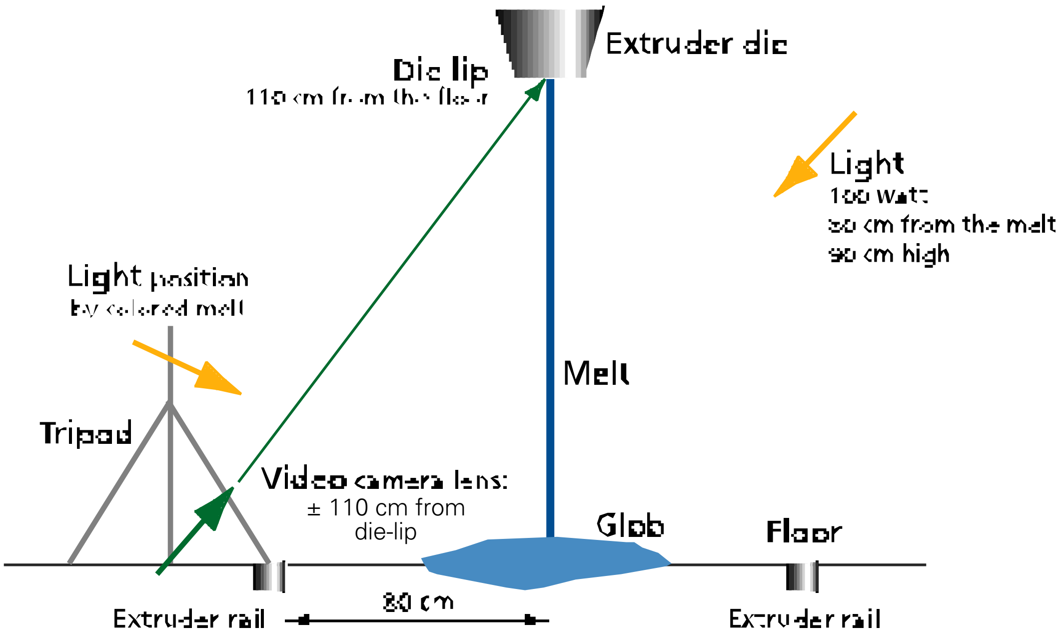
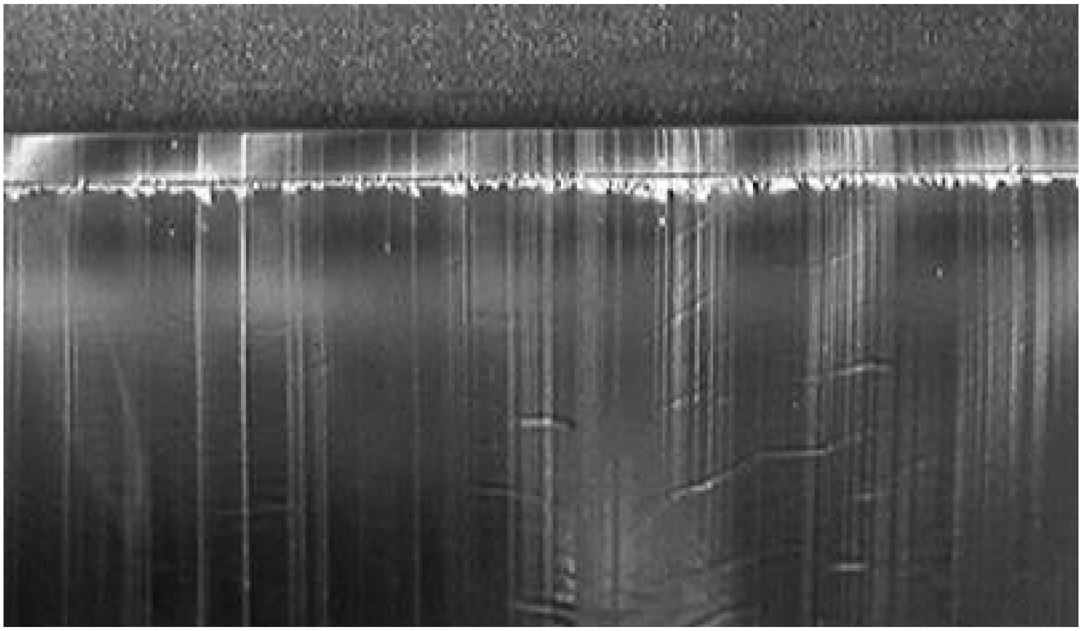


Figure 2b
Die build-up -
Film extrudate



2.2 Estimation of die-swell in the case of a pure polymer

Although useful insights on the die-swell phenomenon can be obtained by a direct measurement of the extrudate diameter, such a technique is not the most appropriate to isolate the influence of the polymer alone on the phenomenon. Indeed, die-swell is time and temperature dependent, which means that extrudate annealing has to be performed in order to reach its fully swollen value. Extruding the polymer into a hot oil with the same density as the melt is an even more reliable method in order to eliminate sagging under the influence of gravity, but then the experiments become extremely cumbersome. Finally, such comparisons are influenced by the presence of processing aids and do not allow the measurement of intrinsic resin characteristics.

In order to overcome all these problems, we preferred to evaluate die-swell from classical rheological data determined by small-amplitude dynamic measurements. Recognizing that die-swell is enhanced by melt elasticity, Tanner [8] calculated die-swell B as :

(1)

$$B = \frac{D}{d} = 0.12 + \left[1 + \frac{1}{8}\left(\frac{N_1}{\tau}\right)^2\right]^{1/6}$$

where d and D are the capillary and filament diameters, N_1 the first normal stress difference characterizing melt elasticity, and s the shear stress at the wall.

This expression considers the swell as the recovery of elastic energy stored in pure shear (capillary of infinite length), which is sufficient for our purpose of ranking different materials. The numerical coefficient of 1/8 has to be replaced by 1/12 in the case of plane flow (slit die). If entrance effects are present, the energy stored in elongation will also become effective, thus resulting in larger values, without modifying the relative variations from one material to another.

The two parameters appearing in Eq. (1) are easily obtained from dynamic moduli G' and G" from two classical empiricism's, namely the Cox-Merz and Laun's rules [9]. The former postulates that steady-state viscosity is identical to complex viscosity determined in oscillatory measurements; it can be re-stated as :

(2)

$$\tau = G''\left[1 + \left(\frac{G'}{G''}\right)^2\right]^{0.5}$$

The latter estimates N_1 from G' and G" as :

(3)

$$N_1 = G'\left[1 + \left(\frac{G'}{G''}\right)^2\right]^{0.7}$$

After some rearrangements, inserting Equations (2) and (3) into (1) yields the final result :

(4)

$$B = 0.12 + \left[1 + \frac{1}{2}\,\frac{1}{[\mathrm{Tan}\delta]^2}\left(1 + \frac{1}{[\mathrm{Tan}\delta]^2}\right)^{0.4}\right]^{1/6}$$

The above expression is a decreasing function of Tand=G"/G', and therefore correctly predicts that B increases with melt elasticity.

2.3 Capillary Rheometry

The performance of fluoropolymer-based processing additives for reducing die build-up can be evaluated by capillary rheometry, performed on a Goettfert capillary rheometer using a flat entry 0.5 mm die with length/diameter ratio of 40/1.

By measuring the apparent shear stress as a function of the apparent shear rates one may notice how PPA significantly reduce the apparent shear stress at a given shear rate. Considering the above, a reduced die-swell and hence less die build-up may be expected especially at more severe process conditions. For a better understanding, one has to consider the velocity profile of a resin being converted without the use of PPA through a profile of simple cross section, as shown in Figure 3. High output rates result in high shear rates at the wall, with a steep gradient through the cross section. On conventional LLDPE's, this leads to significant die-swell, as will be demonstrated.

For a similar output rate, Figure 3 illustrates (a) the appearance of a non-zero slip velocity at the wall, which translates into (b) a lower value for the actual shear rate close to the wall, and so in lower stresses. It has been described in literature [10] that die swell is maximum when critical shear rates are being approached. Since PPA shift the critical shear rates towards higher values, a reduced die-swell may be expected.

To compare different formulations, pictures are taken of the die at the end of each evaluation.

Figure 3a
Die-swell without PPA

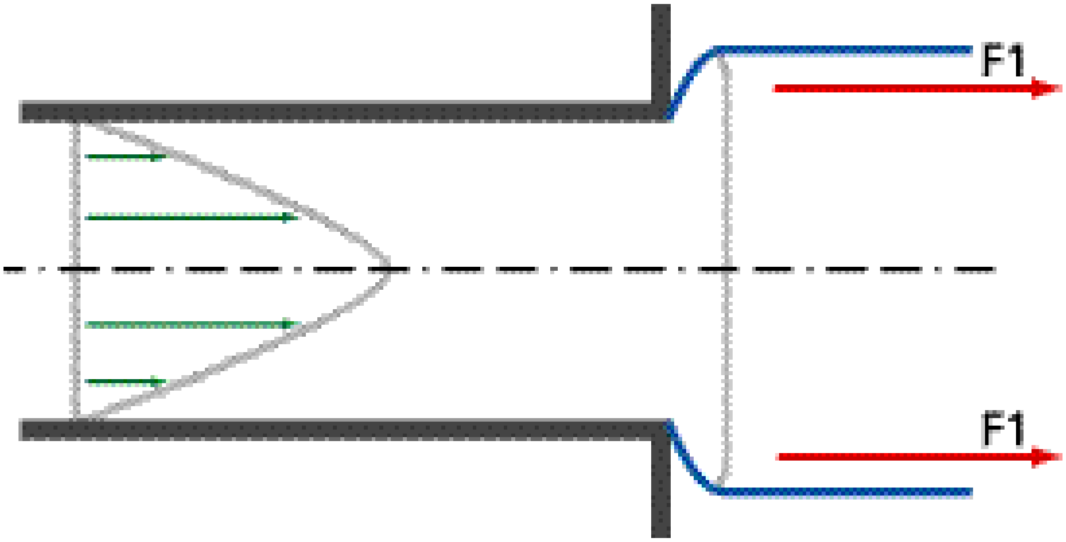
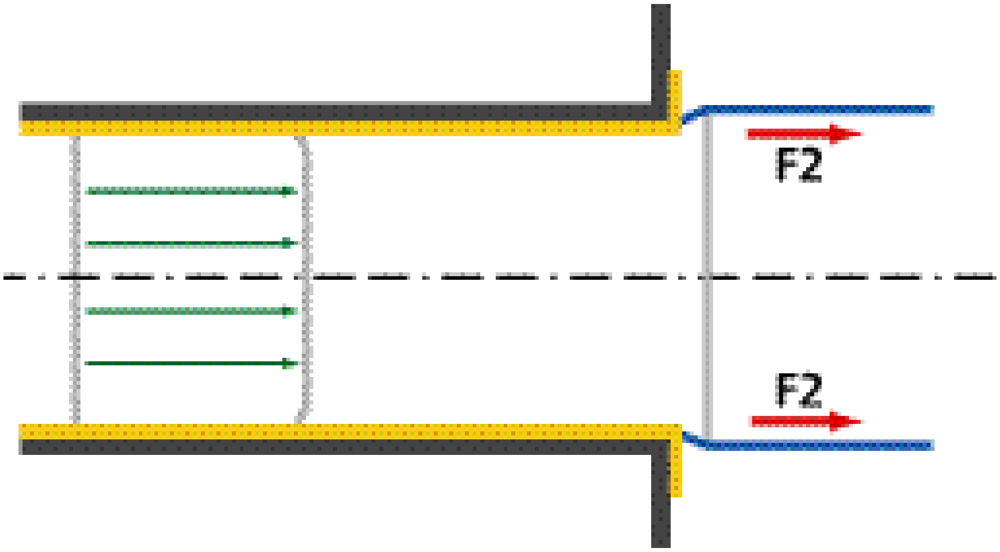


Figure 3b
Die-swell with PPA



3. Experimental results - discussions

3.1 Influence of resin nature on die-swell

Predicted values of die-swell for different polymers, as discussed in chapter 2.2, are listed in Table I, at three different shear rates.

Table I

Sample	Tanδ			Predicted die-swell		
	$100s^{-1}$	$200s^{-1}$	$316s^{-1}$	$100s^{-1}$	$200s^{-1}$	$316s^{-1}$
Z-N LLDPE produced with Unipol technology						
MI=0.5, d=0.918	0.9471	0.8126	0.7283	1.22	1.25	1.28
MI=0.7, d=0.925	1.031	0.8753	0.7684	1.20	1.23	1.27
MI=2.8, d=0.918	1.406	1.156	0.9961	1.16	1.19	1.21
Metallocene mLLDPE produced with Exxpol® technology						
MI=0.75, d=0.927	4.219	3.178	2.651	1.12	1.13	1.13
MI=1.00, d=0.917	4.353	3.366	2.853	1.12	1.13	1.13

It is evident that the metallocene mLLDPE (marketed by Exxon Chemical under the tradename Exceed™), thanks to its narrow molecular weight distribution, has a melt much less elastic than the Ziegler-Natta LLDPE, and offers therefore much lower swell values. These polymers are therefore anticipated to constitute ideal candidates for solving die build-up problems.

3.2 Use of fluoropolymer-based processing additives

Two fluoropolymer-based processing additives were used. One was a copolymer of vinylidene fluoride and hexafluoropropylene containing 10% inorganics as partitioning agent while the other was a proprietary formulation containing a fluoropolymer and a co-additive designed to provide enhanced processing improvements in the presence of mineral additives. These will be referred to in the text as PPA-1 and PPA-2, respectively. Both of them are commercially available as Dynamar™ PPA FX 9613 (PPA-1) and Dynamar™ PPA FX 5920A (PPA-2), and were added to a let down level of 600 ppm through the use of 2% lab prepared masterbatches using a 2.8 MFI LLDPE carrier.

Two types of polymer formulations have been evaluated by capillary rheometry. The properties of those materials are described in Table II.

Table II

Resin	MI (190°C/2.16 kg)	Density (g/cm^3)
LLDPE	0.5	0.918
MDPE	0.17	0.938

A formulation based on an LLDPE resin (0.5 MI, 0.918 g/cm^3) was prepared with 10% of a 60% TiO_2 masterbatch. The TiO_2 was a rutile type pigment produced by the chloride process. The pigment had a non - siloxane organic treatment in combination with Al_2O_3. The masterbatch was produced with a 13 MFI LDPE carrier. To investigate the influence of an extra stabilization package, 1000 ppm of a standard primary antioxidant was incorporated. Compounding of both control and PPA-containing samples was done with a HAAKE torque Rheometer using a Rheomix 3000 mixer with roller blades. The blended resins were ground at ambient temperature prior to use in the capillary rheometer.

Figure 4

Capillary Rheometry data: LLDPE

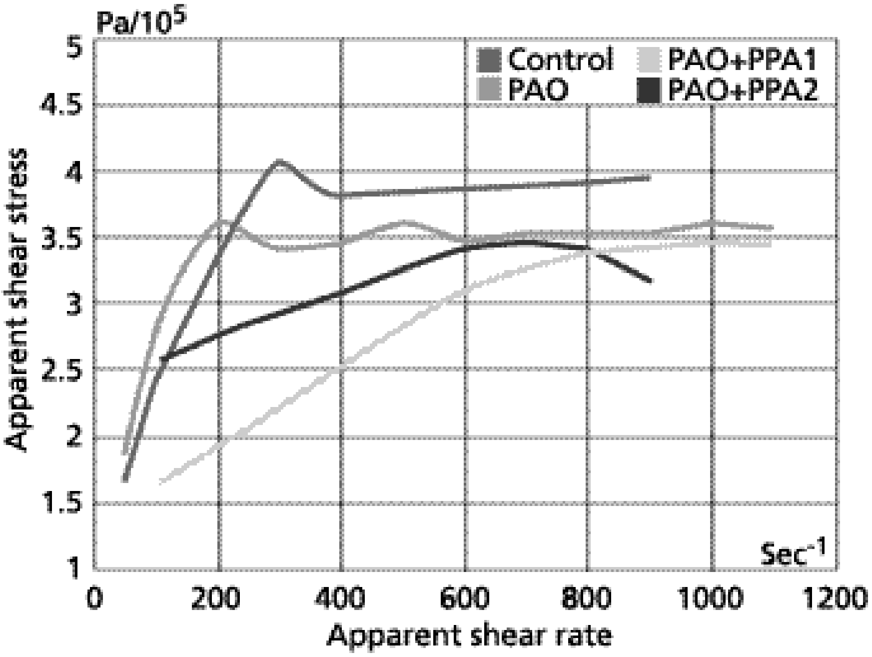


Figure 4 represents the measured apparent shear stresses in function of the apparent shear rates. As one can notice, adding antioxidant has little to no impact on apparent shear stress, the PPA2 reduces the apparent shear stress by 25% and the PPA1 even by 35%.

The results obtained with the MDPE resin were even more pronounced. Shear stress reductions of more than 50% have been recorded.

Table III gives an overview of the extrudate dimensions at different apparent shear rates for the LLDPE formulation. Die-swell indeed increases at elevated shear rates and is significantly reduced in the PPA-containing formulations due to reduced apparent shear stresses at equivalent apparent shear rates.

Table III

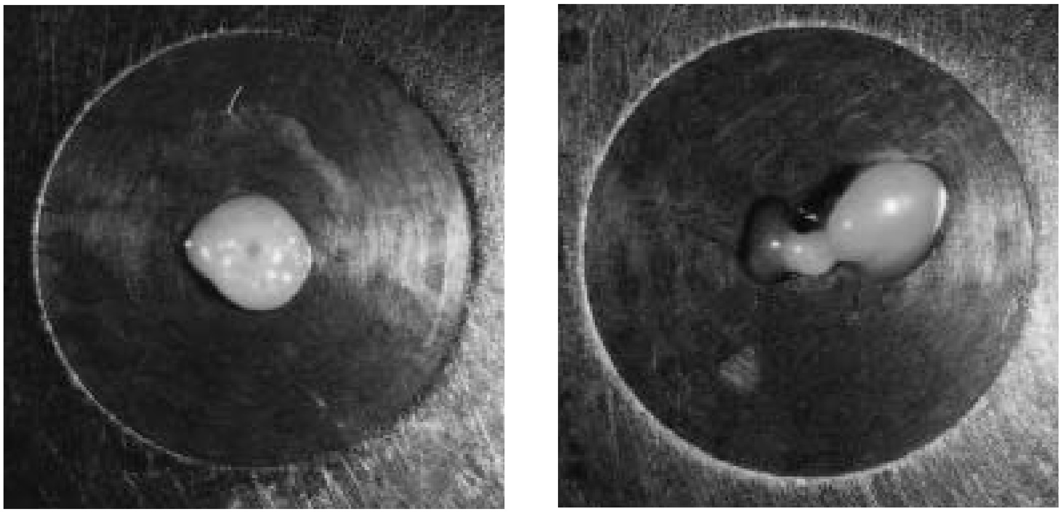
Extrudate dimensions for LLDPE formulations CMF=cyclic melt fracture (observed at critical shear stress), PAO=primary antioxidant

Apparent shear rate (sec^{-1})	Control (mm)	Control + PAO (mm)	Control + PAO + PPA1 (mm)	Control + PAO + PPA2 (mm)
100	0.693	0.641	0.411	0.629
200	0.716	0.750	0.345	0.616
300	CMF	CMF	0.374	0.664
400	CMF	CMF	0.476	0.624
500	CMF	CMF	0.486	0.700

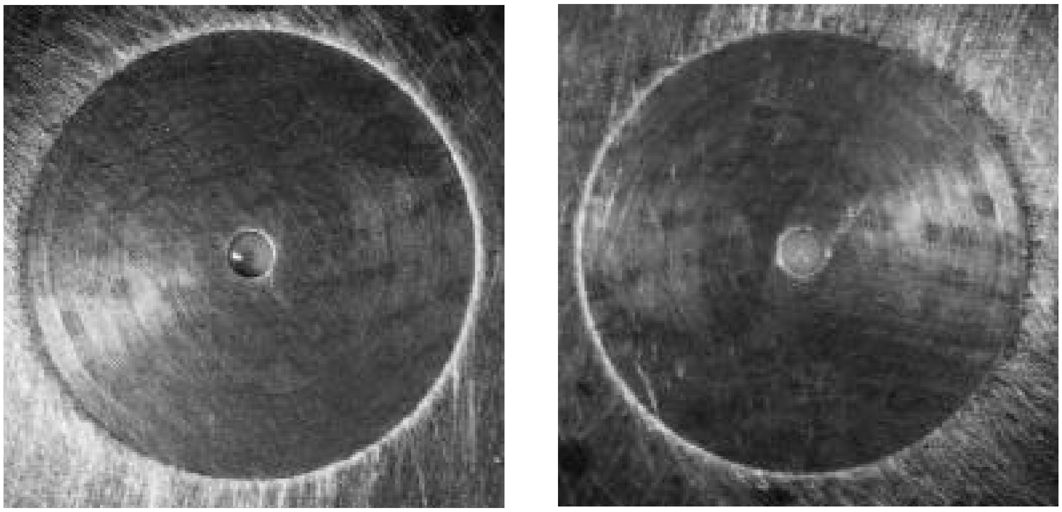
Since it has been demonstrated [2] that die-swell provides a medium for transporting low MW materials and pigments towards the die metal surface, die build-up obtained during each rheological screening was recorded by taking pictures of the die at the end of each session. Each session took about one hour evaluation time. Figure 5 shows significant die build-up when extruding the pigmented MDPE. The use of a proper stabilization package reduces the amount of die build-up due to a reduced flow of degraded materials. PPA1 and PPA2 reduce the amount of die build-up even further due to a reduced die-swell.

Also when evaluating the LLDPE formulations, PPA proved to be extremely efficient in reducing the amount of die build-up during the capillary rheometry session.

Figure 5
Capillary Die pictures
MDPE



MDPE control **MDPE + PAO**



MDPE + PAO + PPA1 **MDPE + PAO + PPA2**

3.3 On-line tests on the lab scale cast line

A demonstration of the dramatic reduction in DBU with metallocene mLLDPE's to DBU formation is that the Exceed™ polymers (ECD 103, 1 MI; ECD 109, 0.75 MI; ECD 202, 2,5 MI; and ECD 301, 3.4 MI) showed no evidence of DBU after 2 hours extrusion at the different temperatures tested (150, 210, and 250°C). In fact much longer extrusion time was possible. Depending on the additive packages, the conventional Ziegler-Natta LLDPE demonstrated sensitivity towards DBU formation. For the same additive package, the lowest MI Z-N LLDPE (0.5 MI) generated DBU within the first hour, the higher MI LLDPE's (0.7, 0.8 and 1 MI) during the second hour, all being extruded at 210°C. The highest MI (2.8 MI) grades were extruded in a wide range of temperatures (150 to 250°C), and showed formation of DBU within 2 hours. See figure 6(a) and 6(b).

Tests have also been carried out on an LDPE (0.2 MI, 0.922 density) in order to assess the influence of processing conditions. The positive impact of blanketing with nitrogen was demonstrated. DBU formation was then delayed by more than 100%. As expected, lowering the die pressure by using a wider die gap (0.6 mm) enabled to run the extruder during one hour before detecting DBU instead of 30 minutes with the narrow die gap (0.25 mm). Increasing the set temperature from 250 to 300°C delayed DBU as well. The positive effect of reducing die-swell at high temperatures more than compensated for the potential influence of polymer degradation as the stabilization package was adequate for those temperatures.

Figure 6(a)
Z-N LLDPE,
2 hours extrusion

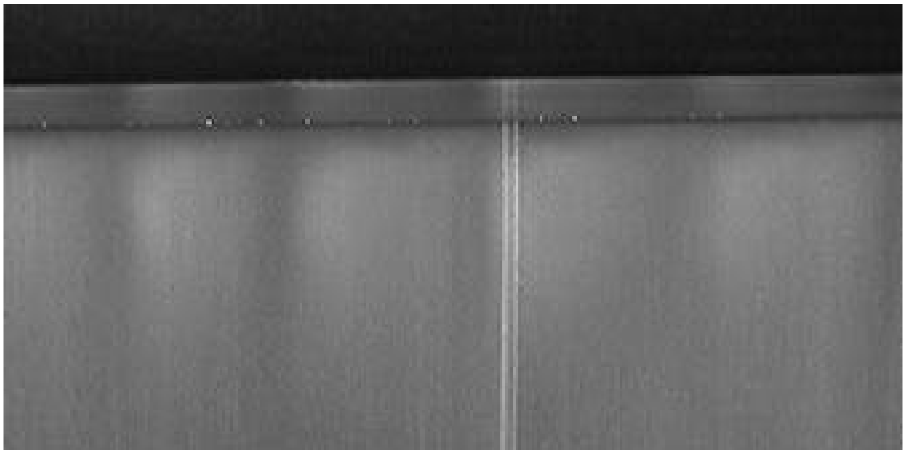
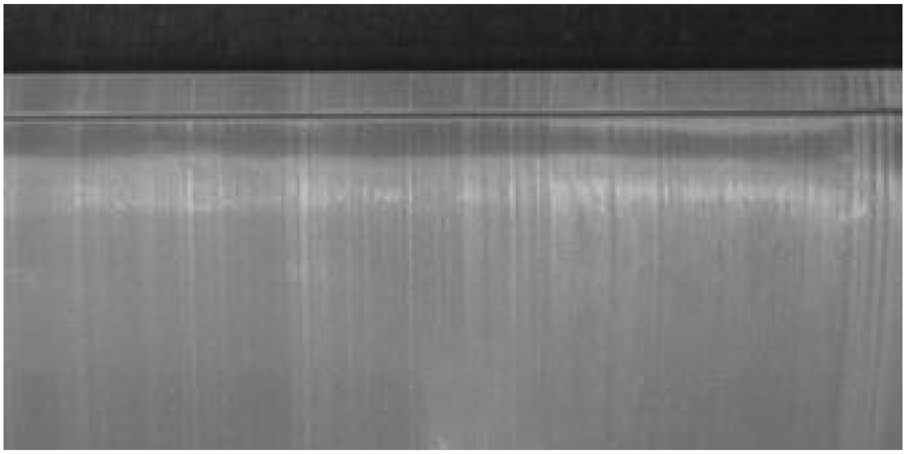


Figure 6(b)
Z-N mLLDPE,
2 hours extrusion



The detrimental effect of moisture has also been verified, since DBU was noticed after 20 minutes when extruding LDPE stored in a highly humid environment, whereas DBU was formed after 45 minutes after drying the polymer. This effect was even more pronounced in the case of antiblock additivated LDPE.

The best use of the test method is demonstrated with pigmented polymers. To exaggerate the effects, tests were done adding 30% of different white MB's in a 0.75 MI LDPE. DBU was generated after a few to 15 minutes for the commodity MB's and only after 1 hour for a "specially developed low die build-up" MB.

Also the effect of PPA was evaluated on the down-sized cast line. The improvement in extrusion performance upon the introduction of PPA additives suggested by the capillary rheometer measurements was verified by running the different formulations described in Table II. The Control formulation has been seen to give DBU problems at a customer's facilities. On the Collin film line, initial DBU was recorded after 5 minutes. Further stabilization of the blend (control + PAO) enabled to run 30 minutes without DBU. Finally, the combination of antioxidant and PPA1 did not show any die build-up after two hours processing. For these comparisons a narrow die gap was maintained.

Figure 7(a)
LLDPE + TiO_2 (6%)

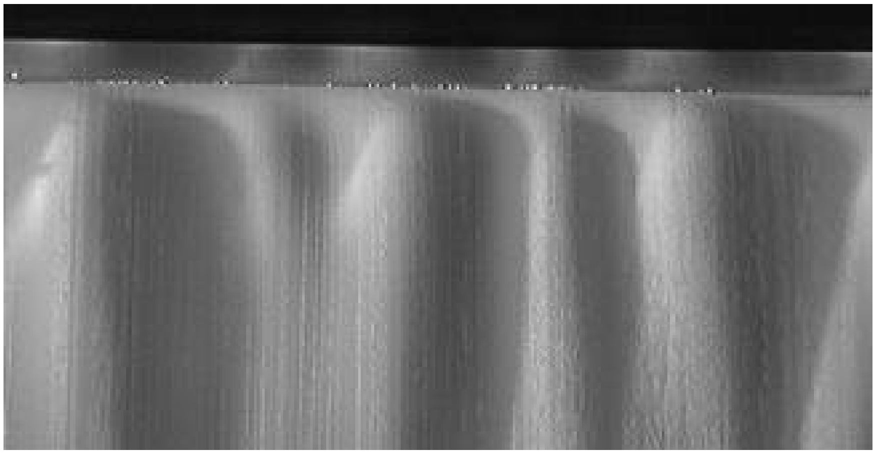
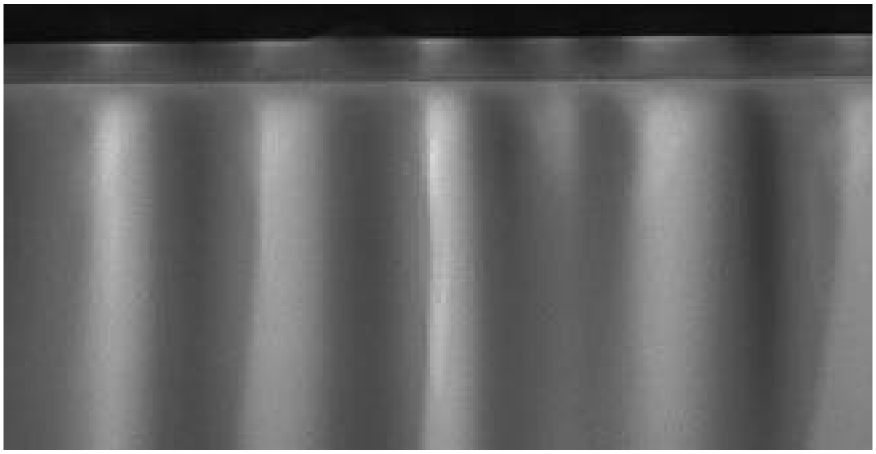


Figure 7(b)
LLDPE + TiO_2 (6%) +
PPA-2 (600 ppm)



The method was also successfully applied on pigmented LDPE, MDPE and PP.

4. Conclusion

A sensitive method has been developed in order to reproduce and quantify die build-up formation. The method helped us in confirming die-swell as a major vehicle of die build-up, suggesting therefore several viable routes in order to minimize the criticality of DBU issues in processing operations.

As compared to traditional Ziegler-Natta products, the new metallocene mLLDPE's (Exceed™) are characterized by narrow molecular weight distribution. Therefore, they show a much reduced melt elasticity at a comparable MI, which results in a low die-swell. In addition, this narrow MWD implies a very small fraction of low molecular weight waxy materials (as an example, 0.71% of hexane extractables were measured for ECD 103 versus 2.8% for a Z-N LLDPE of similar molecular weight and density). Finally, being produced with an efficient and chemically different catalyst technology, they do not require catalyst neutralizer. All these elements contribute to DBU reduction.

The use of appropriate fluoropolymer-based processing additives is an efficient way to minimize DBU. First, such additives migrate to the wall surface, creating a thin layer that favors polymer slip. At a given throughput, this results in a reduction of the stress level, and therefore die-swell as well. Furthermore, the fluoropolymer coating reduces the surface energy of the die wall. Thus, degraded materials and pigments have less propensity to adhere to the metal surface. Together with die swell reduction, the low surface energy will also promote efficient DBU reduction.

5. Appendix 1: References

1. T. Blong, D. Klein, A.V. Pocius, M.A. Strobel, 'The influence of polymer processing additives on the surface, mechanical, and optical properties of LLDPE Blown Film 'TAPPI ‘93 PLC conference.
2. I. Klein, 'Die drool : What causes it, how to avoid it', Plastics World, May 1981.
3. J.D. Gander, A.J. Giacomin, 'Review of die build-up in plastics extrusion' ANTEC ‘96.
4. G. Kress, Kunststoffe, 'Striation on tubular films - Influence on flow channel surfaces' Vol. 65, August 1975.
5. D.E. Priester, G.R. Chapman, 'Reducing die build-up in extrusion applications', DuPont Technical Information.
6. D.E. Priester, 'The effect of die surface characteristics on processing additive performance', ANTEC '94.
7. C.M. Chan, 'Viscosity and the formation of die-drool at the polymer-metal interfaces' International Polymer Processing, Vol. 10, 1995.
8. R.I. Tanner, 'Recoverable elastic strain and swelling ratio', in Rheological Measurement, Ed. A.A. Collyer and D.W. Clegg, Elsevier applied Science.
9. H.M. Laun, 'Predictions of elastic strain of polymer melts in shear and elongation' Journal of Rheology, Vol. 30, 1986.
10. J.A. Brydson, 'Flow Properties of Polymer Melts', Second edition. George Godwin Limited in association with the Plastics and Rubber Institute.

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